DETECTION OF WATER BINDING TO THE OXYGEN EVOLVING COMPLEX USING LOW FREQUENCY SERS

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The oxygen evolving complex (OEC) in Photosystem II (PSII) is a hallmark catalyst for efficiently splitting water to generate molecular oxygen. Much of what is known about the structure of the OEC has been provided by X-ray analysis of PSII at low temperatures, from which the mechanism of water splitting has been inferred. Surface-enhanced Raman scattering (SERS) offers an opportunity to build on our current understanding of this catalytic system as it can provide time-resolved, molecular vibrational information in a physiological environment. With low frequency SERS, we are able to separate the manganese oxide vibrational modes of the OEC from those in a complex, biological environment. With isotopically labelled water, we use SERS to identify water binding to the OEC. Raman spectra calculated by density functional theory support the assignment of water binding to a manganese atom outside of the cuboidal OEC. Detection of water binding sites on the OEC with SERS can not only compliment previous structural studies, but can also provide a powerful platform for in operando mechanistic studies.